13 INFRARED SPECTROSCOPY

13.1 Introduction:

13.1.1 Infrared spectroscopy (IR) is a specific method of identification in most instances and is therefore a desirable analytical tool for the forensic drug chemist. IR may be used to obtain semiquantitative data on known mixtures to express relative percentages, but is not normally used for quantitation.

13.1.2 This method of spectral analysis is based on the molecular vibrational energies of an organic compound. Infrared light containing wavelengths from 4000 cm^{-1} to 400 cm^{-1} is generated and passed through the sample. When the frequency of light matches a frequency of vibration within the molecule, absorption occurs. The absorptions are translated electronically and recorded on a data system. The resulting spectrum will have characteristic bands corresponding to each different vibration among atoms in the molecule.

13.1.3 The IR spectrum of an unknown compound can be compared to the IR spectrum of a known or suitable reference spectrum for confirmation.

13.1.4 The Fourier Transform Infrared Spectrophotometer (FTIR) collects the composite spectrum in the time domain and mathematically transforms it to the frequency domain.

13.1.5 Non-chemical separations (spectral subtraction) may be performed to determine components of a mixture. The components would need to be separated and structural confirmation of the pure compounds done by this or other structural identification techniques, if needed.

13.1.6 Spectra may be collected using an Attenuated Total Reflectance (ATR) accessory and compared to standards also collected utilizing the ATR. These standards may be stored in a user generated library. For unknown compounds, an ATR correction may be utilized in order to search a library of transmission spectra. The uncorrected unknown spectrum would then be compared to that of a known uncorrected standard spectrum.

13.1.7 If unique sample preparation or data reduction techniques are required, consult the Primary Operator for the FTIR.

13.2 Sample Preparation:

13.2.1 Samples should be relatively pure and can be cleaned up by extraction, preparative TLC, recrystallization, or precipitation and filtration, depending upon the quantity and type of contaminants present.

13.2.2 Pure liquid organics can be run neat between two salt (NaCl) plates or using the ATR accessory.

13.2.3 Pure solids can be dissolved in a suitable organic solvent and run in solution cells, mixed with KBr and pressed into a pellet, mixed with a saturated long chain hydrocarbon oil (mulled) or run using the ATR accessory.

13.2.4 Solution Technique:

13.2.4.1 A small amount of the sample is dissolved in a non-polar solvent such as CCl_4 or CS_2. Polar solvents such as MeOH or EtOH should be avoided. Other slightly polar solvents, such as $CHCl_3$, can also be used but will have some interfering absorption bands due to C-H.

13.2.4.2 Oils or dissolved solids may be deposited or "cast" on a salt plate (e.g., standard NaCl window) and placed in the sample beam. (Care must be taken to drive off all residual solvent).

13.2.4.3 The solvent absorption bands may be subtracted from the spectrum. Either a pair of salt plates with the solution solvent or a solution cell (of the same pathlength) containing only solvent can be scanned into the background spectrum.

13.2.5 Gas Techniques:

13.2.5.1 Standard 10 cm gas cells or other similar hardware (e.g., multiple internal reflectance units) can be used.

13.2.6 Mull Technique:

13.2.6.1 The sample is finely ground and suspended in mineral oil (Nujol). A thin film of the suspension is placed between two salt plates.

13.2.7 Pellet Technique:

13.2.7.1 Infrared grade KBr should be kept dry by storing it in a suitable location such as a dessicator.

13.2.7.2 Infrared grade KBr and the sample each must be finely ground. The KBr and sample are mixed by grinding with a mortar and pestle in an approximate ratio of 100 parts KBr to 1 part sample.

13.2.7.3 The mixture is placed in a pellet press to prepare the pellet. A hand press with a 7 mm die or the Hydraulic 13 mm die set may be used. The 7 mm hand press KBr pellet is the preferred preparation technique.

13.2.8 ATR Accessory:

13.2.8.1 Clean the diamond crystal and sapphire anvil surface before and after analysis with acetone or methanol soaked Kimwipes. Methanol takes a slightly longer time to evaporate.

13.2.8.2 For solid samples, cover the center of the crystal with sample. Close and secure the bridge. Press the anvil against the sample by turning the anvil screw clockwise until it spins without further tightening.

13.2.8.3 For liquid samples, place a drop or two of liquid directly onto the ATR crystal. Use enough sample to cover the crystal completely. If the sample is volatile, place the cover over the sampling area to prevent evaporation during analysis. The bridge is not lowered during analysis.

13.2.8.4 If the sample requires an extraction, the sample in an organic solvent may be dropped on a crystal and allowed to evaporate to form a film. The bridge is not lowered during analysis. An o-ring may be used to contain the liquid as it is place on the crystal.

13.3 Gas Phase FTIR via Gas Chromatography

13.3.1 The GC accessory provides FTIR data for samples in solution and vapor phases (head space analysis) using a continuous flow cell. The MCT-A detector scans from 4000 – 650 cm^{-1} and requires cooling with liquid nitrogen prior to analysis.

13.3.2 The spectra produced must be compared to known spectra taken under similar conditions.

13.3.3 GC-FTIR analysis is especially useful for phenethylamines due to the greater number of differences found in the gas phase fingerprint region versus the condensed phase fingerprint region. Also, the gas phase spectra often display more obvious differences between phenethylamines than their GC/MS spectra.

13.3.4 Procedure:

13.3.4.1 The instrument configuration should be set to Series, and the experiment set to GC-FTIR interface.

13.3.4.2 Parameters for the instrumentation are as follows:

- Split 5:1
- Column 30m x 0.32 mm i.d.
- Flow 1.5 – 4.0 mL/min.
- Resolution 8.0
- # of scans 8
- Background 128 scans

13.3.5 An amount of sample (1 – 2 μL) is injected.

13.3.6 After the series is reconstructed and the baseline is corrected, the sample spectrum will be compared to a known gas phase spectrum.

13.4 Acceptance Criteria:

13.4.1 When using FTIR as the primary structural elucidation technique, the sample spectrum should compare favorably with a spectrum of a known standard in both its overall appearance and in the presence and location of the major peaks. Due caution should be exercised when using the similarity index generated by the library search algorithm.

13.4.2 When using FTIR to differentiate cocaine base from cocaine hydrochloride or another salt form where GC/MS has been previously performed, the areas of the spectrum which are different between cocaine base and cocaine hydrochloride should be clear. Other areas may have interfering peaks present that do not mask the "salt form" identity.

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